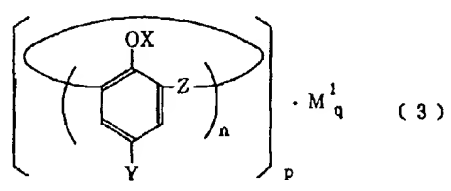


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4. A composition having a catalytic activity for an oxidation by hydrogen peroxide, comprising a cyclic phenol sulfide metal complex represented by formula (3):



(wherein X represents a hydrogen atom, a hydrocarbon group, a carboxyalkyl group, or a carbamoylalkyl group;

Y represents a hydrogen atom, a hydrocarbon group, a halogenated hydrocarbon group, a halogen atom, an acyl group, a hydroxyl group, a carboxyl group, an amido group, an amino group, a nitro group, a cyano group, a chlorosulfonic acid group, an alkoxysulfonyloxy group, or a sulfonic acid group;

Z represents Sm, SO, or SO₂;

m represents an integer of from 1 to 7;

n represents an integer of from 4 to 8;

M represents a transition metal or a rear earth metal; and

p and q represent a composition ratio and an integer of 1 or more)
and a carrier.

5. The composition according to claim 4, wherein the sulfonic acid group represented by Y is sulfonic acid, or a metal salt, an ammonium salt, a (lower alkyl)ammonium salt, a (lower alkanol)ammonium salt or a pyridinium salt of sulfonic acid.

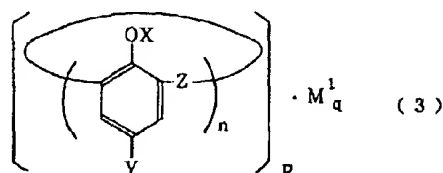
6. A method of oxidation by hydrogen peroxide, comprising, reacting hydrogen peroxide in the presence of the cyclic phenol sulfide metal complex represented by formula (3) described in claim 4.

7. The method according to claim 6, wherein the cyclic phenol sulfide metal complex is mixed with or supported on a solid carrier.

8. A method of analysis for hydrogen peroxide, comprising detecting hydrogen peroxide by reacting the hydrogen peroxide in the presence of the cyclic phenol sulfide metal complex described in claim 4.

9. The method according to claim 8, wherein the cyclic phenol sulfide metal complex is mixed with or supported on a solid carrier.

10. A catalyst composition for hydrolysis of phosphodiester comprising a cyclic phenol sulfide metal complex represented by formula (3):



(wherein X represents a hydrogen atom, a hydrocarbon group, a carboxyalkyl group, or a carbamoylalkyl group;

Y represents a hydrogen atom, a hydrocarbon group, a halogenated hydrocarbon group, a halogen atom, an acyl group, a hydroxyl group, a carboxyl group, an amido group, an amino group, a nitro group, a cyano group, a chlorosulfonic acid group, an alkoxysulfonyloxy group, or a sulfonic acid group;

Z represents Sm, SO, or SO₂;

m represents an integer of from 1 to 7;

n represents an integer of from 4 to 8;

M represents a transition metal or a rear earth metal; and

p and q represent a composition ratio and an integer of 1 or more)

and a carrier.

11. The composition according to claim 10, wherein the sulfonic acid group represented by Y is sulfonic acid, or a metal salt, an ammonium salt, a (lower alkyl)ammonium salt, a (lower alkanol)ammonium salt or a pyridinium salt of sulfonic acid.

12. A method for hydrolyzing phosphodiester, comprising hydrolyzing phosphodiester in the presence of the cyclic phenols sulfide metal complex represented by formula (3) described in claim 10.

13. The method according to claim 12, wherein the cyclic phenol sulfide metal complex is mixed with or supported on a solid support.

14. Use of the cyclic phenol sulfide metal complex represented by formula (3) described in claim 4 as a catalyst for oxidation by hydrogen peroxide.

15. Use of the cyclic phenol sulfide metal complex represented by formula (3) described in claim 10 as a catalyst for hydrolysis of phosphodiester.

Example 9

Production of ion exchanger having cyclic phenol sulfide sulfonic acid cerium complex (X) by preparing ion exchanger having cyclic phenol sulfide sulfonic acid beforehand and then incorporating cerium ion thereinto:

An aqueous solution prepared by dissolving 45.2 mg of the sodium cyclic phenol sulfide sulfonate (II) obtained in Production Example 2 in 50 ml of water was gradually added dropwise, under stirring, to a solution prepared by suspending 500 mg of an anion exchanger (DEAE cellulofine A-500, manufactured by Seikagaku Corporation) in 20 ml of water, followed by further stirring for 1 hour. The ion exchanger obtained was filtered off with a membrane filter, sufficiently washed with water, and then dried in vacuo over P_2O_5 . The color of this ion exchanger having a cyclic phenol sulfide sulfonic acid supported thereon was white.

Subsequently, 10 ml of an aqueous solution prepared by dissolving $Ce(NH_4)_2(NO_3)_6$ in a concentration of 1.0×10^{-2} M (considerably light yellow) was gradually added dropwise, under stirring, to a solution prepared by suspending 500 mg of the ion exchanger described above in 20 ml of water, followed by further stirring for 1 hour. The thus-obtained anion exchanger having a cyclic phenol sulfide sulfonic acid cerium complex (X) was filtered off with a membrane filter, sufficiently washed with water, and then dried in vacuo over

P₂O₅. This anion exchanger having a cyclic phenol sulfide sulfonic acid cerium complex (X) supported thereon had a chocolate color.

The molar ratio of the cyclic phenol sulfide sulfonic acid to cerium ions in the thus-obtained ion exchanger having the cyclic phenol sulfide sulfonic acid cerium complex (X) was calculated from the Ce⁴⁺ ion concentration in 20 ml of the filtrate determined by conducting chelatometric titration with 0.01 M EDTA (ethylenediaminetetraacetic acid ester) solution, and was found to be 1:1.

Example 10

Production of complex of cyclic phenol sulfide sulfonic acid with cerium ion and of ion exchanger having the same:

To an aqueous solution prepared by dissolving 45.2 mg of the sodium cyclic phenol sulfide sulfonate (II) in 50 ml of water, 10 ml of an aqueous solution prepared by dissolving Ce(NH₄)₂(NO₃)₆ in a concentration of 1.0×10^{-2} M was gradually added dropwise under stirring, followed by further stirring for 1 hour. The unreacted cerium ions were removed by adding 200 mg of a cation-exchange resin (Dowex MSC-1, manufactured by Muromachi Kagaku Kogyo Kaisha, Ltd.) to the reaction solution, further stirring the mixture for 1 hour, and filtering off the cation-exchange resin.

The complex (X) obtained is a cyclic phenol sulfide sulfonic acid cerium complex represented by formula (1) wherein $X = H$, $Y = SO_3Na$, $Z = Sm$, $m = 1$, $n = 4$, $p = 1$, $q = 1$, and $M = Ce$.

Subsequently, 50 ml of an aqueous solution of the cyclic phenol sulfide sulfonic acid cerium complex (X) described above was gradually added dropwise to a solution prepared by suspending 500 mg of an anion exchanger (DEAE cellulofine A-500, manufactured by Seikagaku Corporation) in 20 ml of water, followed by further stirring for 1 hour.

The ion exchanger obtained was filtered off with a membrane filter, sufficiently washed with water, and then vacuum-dried on P_2O_5 . The amount of the cerium complex (X) supported was 1×10^{-4} mol per g of the anion exchanger.

Example 11

Deposition of cyclic phenol sulfide sulfonic acid cerium complex (X) on chitosan:

In 175 ml of 0.05 N hydrochloric acid solution was dissolved 0.5 g of chitosan (Chitosan 500, manufactured by Seikagaku Corporation). Thereafter, 280 ml of water was added to obtain an aqueous chitosan solution. A solution prepared by dissolving 45.2 mg of the sodium cyclic phenol sulfide sulfonic acid (II) obtained in Production Example 2 in 50 ml of water was gradually added dropwise to the

chitosan solution with stirring at room temperature, followed by further stirring for 1 hour. An aqueous sodium bicarbonate solution was added to the resultant solution so as to make it neutral. The precipitate yielded was filtered off with a membrane filter, sufficiently washed with water, and then dried in vacuo over P_2O_5 . The color of this chitosan having a cyclic phenol sulfide sulfonic acid supported thereon was white. Subsequently, 10 ml of an aqueous solution prepared by dissolving $Ce(NH_4)_2(NO_3)_6$ in a concentration of 1.0×10^{-2} M was gradually added dropwise, under stirring at room temperature, to 20 ml of a solution prepared by suspending 0.5 g of the chitosan having a cyclic phenol sulfide sulfonic acid supported thereon in water, followed by further stirring for 1 hour. The thus-obtained chitosan having a cyclic phenol sulfide sulfonic acid cerium complex (X) was filtered off with a membrane filter, sufficiently washed with water, and then dried in vacuo over P_2O_5 . This chitosan having a cyclic phenol sulfide sulfonic acid cerium complex (X) supported thereon had a chocolate color. Incidentally, the amount of the cerium complex (X) supported was 5.0×10^{-5} mol per 0.5 g of the chitosan.

Example 12

Catalytic activity of anion exchanger obtained in Example 10 having cyclic phenol sulfide sulfonic acid cerium complex (X) in hydrolysis of phosphodiester:

Sodium bis(p-nitrophenyl) phosphate (BNPP) was used as a phosphodiester. The presence of a p-nitrophenolate (λ_{max} : 400 nm) as a hydrolyzate thereof in a reaction liquid was determined by determining the absorbance at 400 nm.

To a mixed solution consisting of 3 ml of a 2×10^{-4} M solution of BNPP and 3 ml of a buffer solution, 20 ml of the ion exchanger having a cyclic phenol sulfide sulfonic acid cerium complex (X) was added, followed by shaking at room temperature for 1 hour. The pH range was from 4 to 11. The buffer solution was prepared using 0.1 M CH_3COOH and 0.1 M CH_3COONa for pH ranges of from 4 to 6, prepared using 1/30 M KH_2PO_4 and 1/30 M Na_2HPO_4 for a pH of 7, or prepared using 0.1 M NH_4OH and 0.1 M NH_4Cl for pH ranges of from 8 to 11. Subsequently, the ion exchanger having a cyclic phenol sulfide sulfonic acid cerium complex (X) was filtered out of the reaction liquid with a membrane filter. The solution obtained was examined for absorbance at 400 nm.

The results are shown in Fig. 3.

As a result, absorption at 400 nm was observed, which indicated that the BNPP had been hydrolyzed in the presence of the anion exchanger having a cyclic phenol sulfide

sulfonic acid cerium complex (X) and a p-nitrophenolate had been yielded. The absorption was maximum at around pH = 9.

Example 13

Catalytic activity of anion exchanger obtained in Example 9 having cyclic phenol sulfide sulfonic acid cerium complex (X) in hydrolysis of phosphodiester:

Absorbance at 400 nm was determined in the same manner as in Example 12, except that the anion exchanger obtained in Example 9 having a cyclic phenol sulfide sulfonic acid cerium complex (X) was used in place of the anion exchanger obtained in Example 10 having a cyclic phenol sulfide sulfonic acid cerium complex (X).

As a result, even when the anion exchanger obtained in Example 9 having a cyclic phenol sulfide sulfonic acid cerium complex (X) was used, the same absorbance was obtained as in the case where the anion exchanger obtained in Example 10 having a cyclic phenol sulfide sulfonic acid cerium complex (X) was used.

It can be seen that the same ion exchanger having a cyclic phenol sulfide metal complex was prepared in the case where the cyclic phenol sulfide metal complex was formed beforehand and the ion exchanger was prepared thereafter and in the case where an ion exchanger having a cyclic phenol

sulfide was prepared first and the metal was incorporated thereafter.

Example 14

Catalytic activity of chitosan obtained in Example 11 having cyclic phenol sulfide sulfonic acid cerium complex (X) supported thereon in hydrolysis of phosphodiester:

Absorbance at 400 nm was determined in the same manner as in Example 12, except that the chitosan obtained in Example 11 having a cyclic phenol sulfide sulfonic acid cerium complex (X) supported thereon was used in place of the anion exchanger used in Example 12 having a cyclic phenol sulfide sulfonic acid cerium complex (X).

As a result, even when the chitosan having a cyclic phenol sulfide sulfonic acid cerium complex (X) supported thereon was used, the same results were obtained as the absorbance obtained in the case where the anion exchanger having a cyclic phenol sulfide sulfonic acid cerium complex (X) was used in Example 12.

Example 15

Reproducibility of catalytic activity of anion exchanger having cyclic phenol sulfide sulfonic acid cerium complex (X) in hydrolysis of phosphodiester:

An anion exchanger having a cyclic phenol sulfide sulfonic acid cerium complex (X) was prepared in the same manner as in Example 9, except that the metal was incorporated under conditions of 60°C in place of room temperature.

This ion exchanger having a cyclic phenol sulfide sulfonic acid cerium complex (X) was repeatedly used to repeatedly make determination five times at a pH of 9 by the same method as in Example 12.

The results are shown in Fig. 4.

As a result, the absorbances observed in all the five measurements were almost the same. The same activity was reproduced even when the ion exchanger having a cyclic phenol sulfide sulfonic acid cerium complex (X) was repeatedly used. Consequently, the anion exchanger having a cyclic phenol sulfide sulfonic acid cerium complex (X) can withstand repetitions of use as a catalyst for hydrolysis of phosphodiester.